Mass spectra of liquid crystals. V.Cyclohexyl and phenyl esters of cyclohexanecarboxylic and benzoic acids

ORGANIC MASS SPECTROMETRY, VOL. 26, 142–146 (1991)

Mass Spectra of Liquid Crystals

V.†—Cyclohexyl and Phenyl Esters of Cyclohexanecarboxylic and Benzoic Acids

P. A. Leclercq‡
Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

H. M. van den Bogaert
Philips Research Laboratories, PO Box 80 000, 5600 JA Eindhoven, The Netherlands

The 70 eV electron impact mass spectra of 38 cyclohexanecarboxylate and 15 benzoate derivatives are presented. This part includes data on six substituted cyclohexyl and 47 derivated phenyl esters, including eleven alkoxyphenyl and 17 dicyanoalkoxyphenyl esters. Based on the observed peak shifts by various substituents, the elemental formulae of the main fragment ions are rationalized.

INTRODUCTION

Liquid crystals have been the subject of considerable study during the last decade. Such compounds, blended in multi-component mixtures, have found extensive application in opto-electronic devices such as liquid crystal displays (LCDs). Surprisingly, there are only a few reports on the mass spectrometry of these compounds. In this paper, the mass spectra of various classes of esters are presented. Each class has different material properties which are used to tune the nematic phase of LCDs for specific applications. Cyclohexyl cyclohexanoates (class I) are esters with small optical anisotropy. These low-birefringence materials increase the viewing angle of LCDs. Class II esters have found wide use because of their low viscosity and their wide nematic temperature ranges. The 2,3-dicyanophenyl esters of classes III and IV have strong negative dielectric anisotropy. These components are used in electrically controlled birefringence (ECB) LCDs. The ECB LCDs offer higher contrast, a wider viewing angle and a more stable grey scale than twisted nematic (TN) displays. Fluorinated phenyl benzoates (class V) are applied to decrease LCD response times.

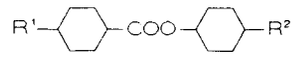
The mass spectra of the five classes of esters are collated in Tables 1–7. In the discussion of the spectra the 'peak shift technique' is employed to deduce the nature of the various fragment ions. In this technique, use is made of the shifts in m/z values by different substituents within a class of compounds. It should be emphasized, however, that the ion structures given are not to be taken literally, because accurate mass measurements were not carried out.

EXPERIMENTAL

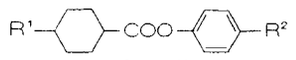
Gas chromatographic/mass spectrometric analyses were carried out under conditions reported previously.[1] For the determination of the molecular masses of the various esters, positive ion chemical ionization mass spectra were acquired on a Finnigan 4000 quadrupole instrument (Finnigan, San Jose, CA, USA). Methane and ammonia were used as reagent gases.

RESULTS AND DISCUSSION

The mass spectra of six alkylcyclohexyl esters of alkyl(bi)cyclohexylcarboxylic acids **1–6** (class I) are condensed in Table 1.



Class I



Class II

To our knowledge, none of these spectra have been reported previously. Molecular ions are absent in all instances. The only peaks indicative for R^2 are found at m/z $(81 + R^2)$, corresponding to the odd-electron alkylcyclohexene ions $[C_6H_9R^2]^{+\cdot}$. The heaviest ions found in the mass spectra of these compounds are from the protonated free acids, $[R^1C_6H_{10}C(OH)_2]^+$ at m/z $(128 + R^1)$. These ions lose one and two molecules of water, resulting in peaks at m/z $(110 + R^1)$ and $(92 + R^1)$, respectively. Loss of CO from the carbonyl cation at m/z $(110 + R^1)$ leads to peaks at m/z $(82 + R^1)$ from the alkylcyclohexyl ions $[R^1C_6H_{10}]^+$. The spectra of the cyclohexyl esters are dominated by abundant low-mass ion series.

The electron impact (EI) spectra of 21 substituted phenyl esters of (bi)cyclohexylcarboxylic acid derivatives **7–27** (class II) are listed in Tables 2–4. The mass spectrum of **18** has been published before.[2] The spectrum of the pentoxyphenyl ester of propylcyclohexanecarboxylic acid, a homologue of **23** and **24**, has also been reported.[3] The origin of two to six characteristic ions in the spectra of **15–19** was rationalized previously,

† For Parts I and IV, see Refs. 1 and 6.
‡ Author to whom correspondence should be addressed.

0030–493X/91/030142–05 $05.00

Received 29 August 1990
Revised manuscript received 15 November 1990
Accepted 16 November 1990

Table 1. Relative abundances of characteristic ions in the EI mass spectra of cyclohexanecarboxylic acid cyclohexyl ester derivatives (class I)[a]

				m/z											
No	R^1	R^2	RMM	128 + R^1	110 + R^1	109 + R^1	92 + R^1	82 + R^1	81 + R^2	127	125	123	111	109	97
1	Pr	Pr	294	100	5	—	7	[d]	50	—	25[e]	—	—	7	4
2	Pe	Pr	322	98	4	—	6	3	61	—	—	—	8	9	27
3	X[c]	Pr	376	60	3	3	23	5	63	10	23[e]	13	14	23	11
4	Y[c]	Pr	390	60	3	3	16	4	65	13	22[e]	13	6	21	17
5	X[c]	Pe	404	97	5	5	32	10	70	14	17	17	31	35	71
6	Y[c]	Pe	418	92	4	4	24	3	66	16	12	18	17	31	76

							m/z								
No.	96	95	83	82	81	79	71	69	67	57	55	54	43	41	Base peak[b]
1	—	1	40	82	54	7	1	82	20	24	13	15	7	26	171
2	13	18	54	100	55	8	7	60	28	18	56	16	27	46	82
3	12	24	61	99	71	15	2	100	42	20	71	19	20	50	69
4	16	24	77	100	71	14	3	84	39	23	74	18	20	48	82
5	96	33	79	60	95	19	11	83	54	23	100	24	35	54	55
6	100	32	85	52	90	16	13	56	54	24	92	20	37	52	96

[a] Pr = *n*-propyl, Bu = *n*-butyl, Pe = *n*-pentyl, C_6H_{10} = 1,4-cyclohexyl.
[b] *m/z* of base peak.
[c] X = Pr-C_6H_{10}, Y = Bu-C_6H_{10}.
[d] Coincides with *m/z* 125.
[e] Including isotopic contribution of *m/z* (81 + R^2).

Table 2. Relative abundances of characteristic ions in the EI mass spectra of cyclohexanecarboxylic acid phenyl ester derivatives (class II)[a]

					m/z									
No.	R^1	R^2	RMM	$M^{+\cdot}$	110 + R^1	109 + R^1	93 + R^2	82 + R^1	93 + A[c]	111	109	97	96	95
7	Pe	F	292	1	30	—	28	26	28	29	5	100	—	14
8	Hp	F	320	1	30	—	34	27	34	80	8	100	—	17
9	Pe	Me	288	7	24	46	93	22	30	—	—	100	10	20
10	Bu	Pr	302	6	16	46	60	26	81	1	8	35	7	11
11	Bu	Bu	316	6	17	49	80	29	100	—	—	21	8	—
12	Bu	Pe	330	5	16	47	77	28	87	1	8	34	7	9
13	Pe	Pe	344	6	18	53	96	22	100	22	11	94	9	15

						m/z							
No.	91	83	81	79	77	71	69	67	57	55	43	41	Base peak[b]
7	—	79	26	7	2	23	36	23	28	64	25	45	97
8	—	86	39	9	3	17	59	37	53	76	40	63	97
9	12	9	9	31	30	20	10	21	8	8	13	5	97
10	8	100	27	11	12	5	31	24	27	52	16	55	83
11	—	69	—	—	5	6	—	4	16	3	7	6	107
12	8	100	26	9	10	6	29	21	28	46	16	42	83
13	9	64	31	10	10	19	29	26	20	51	32	46	107

[a] Me = methyl, Pr = *n*-propyl, Bu = *n*-butyl, Pe = *n*-pentyl.
[b] *m/z* of base peak.
[c] A = 14 (CH_2, compounds **9–13**) or 19 (F, **7** and **8**).

and their masses have been published.[2–4] These literature data are in agreement with our findings and support the structure assignments to the main fragment ions.

With the exception of the bicyclohexylcarboxylic acid esters **25–27**, the molecular ions are present in all instances, albeit with low abundances. In the spectra of **7–13** and **25–27**, peaks at *m/z* (110 + R^1) from $[R^1C_6H_{10}CO]^+$ are higher than those in the spectra of the cyclohexyl esters **1–6**, whereas these peaks are virtually absent in those of the alkoxyphenyl esters **14–24**. Odd-electron ions 1 u lower in mass are found exclusively in the spectra of the alkylphenyl esters **9–13** (Table 2). The ions $[HOC_6H_4R^2]^{+\cdot}$ are responsible for the base peaks at *m/z* (93 + R^2) in the spectra of the alkoxyphenyl esters (Table 3). These spectra also contain large peaks at *m/z* 110, corresponding to $[HOC_6H_4OH]^{+\cdot}$, whenever the alkoxy group is larger than methoxy. Similarly, tropylium ions $[HOC_6H_4CH_2]^+$ cause peaks at *m/z* 107 in the spectra

Table 3. Relative abundances of characteristic ions in the EI mass spectra of cyclohexanecarboxylic acid alkoxyphenyl ester derivatives (class II)[a]

					m/z													
No.	R^1	R^2	RMM	$M^{+\cdot}$	110 + R^1	93 + R^2	82 + R^1	110	109	97	83	81	69	67	57	55	43	41	Base peak[b]
14	Bu	OH	276	11	1	100	—	[c]	88	15	20	6	14	8	6	26	20	31	110
15	Pr	OMe	276	2	—	100	13[d]	—	10	—	10	6	17	4	3	11	3	13	124
16	Bu	OMe	290	2	—	100	2	—	9	6	17	6	6	5	4	12	3	12	124
17	Pe	OMe	304	1	—	100	—	—	9	12	11	7	7	6	3	14	6	13	124
18	Pr	OEt	290	2	—	100	5	30	7	—	12	10	20	5	4	13	4	13	138
19	Bu	OEt	304	2	—	100	10[d]	27	6	6	17	10	7	5	4	13	3	10	138
20	Pe	OEt	318	1	—	100	—	25	7	11	10	9	7	6	3	14	7	11	138
21	Bu	OPr	318	2	1	100	2	55	10	8	21	12	9	9	6	21	16	25	152
22	Et	OBu	304	2	1	100	27[d]	89	12	—	1	11	42	10	8	24	4	36	166
23	Pr	OBu	318	1	—	100	6	69	—	—	13	8	22	6	8	15	3	22	166
24	Bu	OPe	346	1	1	100	2	78	—	9	23	11	12	9	7	23	24	24	180

[a] Me = methyl, Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, Pe = *n*-pentyl.
[b] *m/z* of base peak.
[c] See *m/z* (93 + R^2).
[d] Including isotopic contributions of peaks at 1 u less.

Table 4. Relative abundances of characteristic ions in the EI mass spectra of bicyclohexylcarboxylic acid phenyl ester derivatives (class II)[a]

							m/z								
No.	R^1	R^2	RMM	110 + R^1	93 + R^2	82 + R^1	179	165	153	151	139	137	125	123	111
25	X[c]	F	346	54	41	76	—	5	—	22	—	34	63	41	100
26	Z[c]	F	374	18	30	20	5	8	21	16	45	27	20	29	38
27	Z[c]	Pe	426	37	—	53	8	12	23	19	85	31	36	28	51

						m/z							
No.	109	97	95	83	81	79	69	67	57	55	53	43	41	Base peak[b]
25	43	55	43	83	65	20	84	44	22	78	10	16	58	111
26	31	82	43	100	68	21	44	54	29	86	10	38	65	83
27	31	100	34	76	54	14	78	46	28	80	7	15	47	97

[a] Pr = *n*-propyl, Pe = *n*-pentyl, C_6H_{10} = 1,4-cyclohexyl.
[b] *m/z* of base peak.
[c] X = Pr-C_6H_{10}, Z = Pe-C_6H_{10}.

of the alkylphenyl esters. Alkylcyclohexyl ions $[R^1C_6H_{10}]^+$ give peaks at *m/z* (82 + R^1), which are higher in the spectra of **7–13** and **25–27** than in those of the alkoxyphenyl (**14–24**) and alkylcyclohexyl esters (**1–6**). Abundant lower mass ions are found in the spectra of esters **7–13** and **25–27**. while the corresponding peaks are less intense in those of the alkoxyphenyl esters.

The spectra of the bicyclohexylcarboxylic acid phenyl esters **25–27** (Table 4) contain cycloalkyl and cycloalkenyl ions up to *m/z* (110 + R^1). The fluorophenyl esters **25** and **26** produce additional ions by the loss of H_2O from $[R^1C_6H_{10}CO]^+$, resulting in small peaks at *m/z* (92 + R^1): *m/z* 217 (5%) and 245 (2%), respectively (not included in Table 4).

New EI mass spectra of eleven 4-alkoxy-2,3-dicyanophenyl esters of 4-alkylcyclohexylcarboxylic acids **28–38** (class III) are presented in Table 5. The spectrum of the pentyloxydicyanophenyl hexylcyclohexanoate **38** is also shown in Fig. 1.

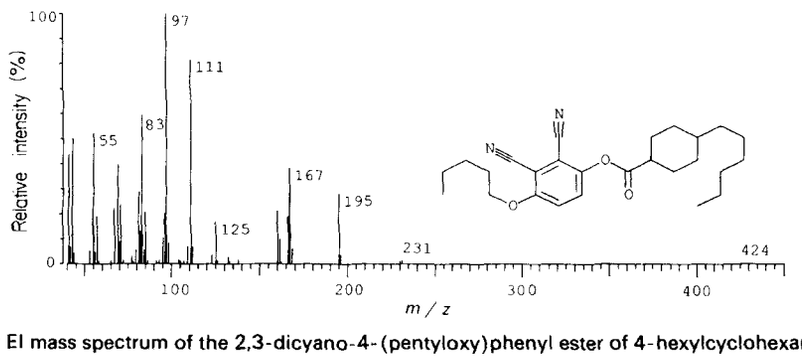
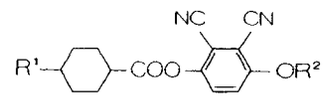
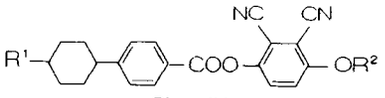


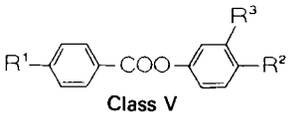
Figure 1. 70 eV EI mass spectrum of the 2,3-dicyano-4-(pentyloxy)phenyl ester of 4-hexylcyclohexanecarboxylic acid (**38**).



Class III



Class IV



Class V

Molecular ions are absent, or have abundances <1%. Peaks at m/z (159 + R^2), corresponding to ions $[HOC_6H_2(CN)_2OR^2]^{+\cdot}$, are small. This contrasts strikingly with the spectra of the (unsubstituted) alkoxyphenyl esters (Table 3), where the corresponding *p*-hydroxyphenylalkyl ethers represent the base peaks. The peaks at m/z (110 + R^1) and (82 + R^1), however, are much larger than in those spectra. These peaks again correspond to the ions $[R^1C_6H_{10}CO]^+$ and $[R^1C_6H_{10}]^+$, respectively. The latter is accompanied by a peak from the alkylcyclohexene ions $[R^1C_6H_9]^{+\cdot}$ at m/z (81 + R^1). Peaks at m/z 160 are characteristic of alkoxydicyanophenyl esters, and arise from the ions $[HOC_6H_2(CN)_2OH]^{+\cdot}$. The ethoxyphenyl derivatives **28**, **33** and **36** also yield peaks at m/z 159, while these peaks are completely absent in the spectra of the other compounds. This phenomenon is not easily rationalized.

Lower mass cycloalkyl fragment ions are abundant. Peaks characteristic of R^1 are found at m/z 82 (R^1 = Pr and Hx), 96 (R^1 = Bu) and 124 (R^1 = Pe). The hexylcyclohexanoate derivatives **36–38** also give peaks at m/z 125 and 85, while peaks at m/z 95, 81, 71 and 67 are larger in the spectra of **33–38** than in those of compounds with R^1 < Pe. The underlying fragmentation mechanisms are not yet understood.

The EI mass spectra of six alkoxydicyanophenyl esters of alkylcyclohexylbenzoic acids **39–44** (class IV) are condensed in Table 6. Mass spectra of these esters have not been published, but the occurrence of very stable carbonyl ions as base peaks in the spectra of some alkylbenzoates and alkylcyclohexylbenzoates has been reported.[2,5] In agreement with these findings, peaks at m/z (186 + R^1), corresponding to $[R^1C_6H_{10}C_6H_4CO]^+$, represent about 50% of the total ion currents. Molecular ions, and ions $[HOC_6H_2(CN)_2OR^2]^{+\cdot}$, are completely absent. Peaks at m/z 160, however small, are characteristic of these esters, as described for **28–38**. Again, peaks at m/z 159 are found exclusively in the spectra of the ethoxyphenyl esters **39** and **42**. Ions of m/z 131 and 115 come from

Table 5. Relative abundances of characteristic ions in the EI mass spectra of alkylcyclohexylcarboxylic acid dicyanoalkoxyphenyl esters (class III)[a]

				m/z												
No.	R^1	R^2	RMM	160 + R^2	159 + R^2	110 + R^1	82 + R^1	81 + R^1	160	159	125	111	109	104	97	96
28	Pr	Et	340	—	4	32	79	14	23	8	[c]	—	3	5	—	3
29	Pr	Bu	368	—	1	32	100	18	25	—	[c]	—	3	2	1	3
30	Pr	Pe	382	1	1	32	100	—	20	—	[c]	—	2	2	4	3
31	Bu	Bu	382	1	1	23	37	11	19	—	5	—	3	2	34	10
32	Bu	Pe	396	—	—	24	47	13	14	—	—	—	3	1	33	10
33	Pe	Et	368	—	—	28	35	10	25	10	8	25	6	—	100	—
34	Pe	Bu	396	—	—	26	37	13	27	—	2[d]	26	5	3	100	—
35	Pe	Pe	410	1	—	25	40	14	19	—	2[d]	28	6	—	100	—
36	Hx	Et	382	4	5	30	38	14	40	14	29	88	10	7	100	2
37	Hx	Bu	410	2	2	27	41	14	32	—	17	79	8	2	100	—
38	Hx	Pe	424	1	1	28	39	19	21	—	17	82	7	2	100	20

							m/z								
No.	95	85	83	82	81	79	71	69	67	57	55	53	43	41	Base peak[b]
28	5	—	54	16	19	6	—	100	17	22	42	7	12	37	69
29	5	—	52	16	19	4	1	87	14	30	37	5	10	44	125
30	5	—	55	17	17	4	5	83	15	25	40	5	30	41	125
31	5	—	100	—	21	4	5	28	13	32	41	4	11	41	83
32	6	—	100	—	19	4	8	25	11	24	36	4	29	32	83
33	12	3	71	—	27	7	19	38	22	19	56	7	23	42	97
34	11	3	77	—	23	5	19	23	19	28	45	6	13	39	97
35	10	3	62	—	21	5	22	29	15	19	40	5	38	35	97
36	14	21	86	18	35	9	16	51	34	31	67	10	31	53	97
37	12	19	66	12	28	6	16	40	22	33	54	6	28	53	97
38	11	21	60	13	29	6	24	40	22	19	52	6	50	44	97

[a] Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, Pe = *n*-pentyl, Hx = *n*-hexyl, C_6H_4 = 1,4-phenyl, C_6H_{10} = 1,4-cyclohexyl.
[b] m/z of base peak.
[c] See m/z (81 + R^1).
[d] At 1 u lower.

Table 6. Relative abundances of characteristic ions in the EI mass spectra of alkylcyclohexylbenzoic acid dicyanoalkoxyphenyl esters (class IV)[a]

				m/z													
No.	R^1	R^2	RMM	186 $+R^1$	184 $+R^1$	160	159	131	129	115	105	103	91	77	55	43	41	Base peak[b]
39	Et	Et	402	100	1	3	2	6	1	4	4	3	5	4	2	—	3	215
40	Et	Bu	430	100	1	2	—	5	1	3	3	2	5	2	2	—	5	215
41	Et	Pe	444	100	1	1	—	5	2	3	3	2	4	3	2	5	4	215
42	Bu	Et	430	100	—	4	3	8	4	6	7	4	7	4	3	2	4	243
43	Bu	Bu	458	100	2	3	—	7	2	4	4	3	5	4	3	1	6	243
44	Bu	Pe	472	100	2	3	—	8	2	4	5	3	5	3	3	7	5	243

[a] Et = ethyl, Bu = *n*-butyl, Pe = *n*-pentyl.
[b] *m/z* of base peak.

Table 7. Relative abundances of characteristic ions in the EI mass spectra of various benzoic acid phenylester derivatives (class V)[a]

					m/z									
No.	R^1	R^2	R^3	RMM	104 $+R^1$	92 $+R^2$ $+R^3$	131	76 $+R^1$	104 $+A^c$	115	105	103	92	91
45	Et	CN	H	251	100	1	—	13	1	—	[d]	7	—	1
46	Pr	CN	H	265	100	[d]	—	8	6	3	—	2	1	20
47	Pr	CN	F	283	100	1	1	8	6	2	—	2	1	20
48	MeO	Et	H	256	100	—	—	7	1	—	—	—	10	3
49	YO[e]	F	H	384	15	1	—	—	100	—	—	—	4	—
50	X[e]	F	H	340	100	4	11	—	4	10	8	6	—	10
51	X[e]	CN	F	365	100	2	10	—	3	8	7	6	1	9
52	X[e]	Z[e]	H	423	100	1	5	—	1	3	3	2	—	4
53	Y[e]	Z[e]	H	451	100	1	7	—	3	3	4	2	—	6

						m/z							
No.	90	89	83	79	77	69	64	63	55	51	43	41	Base peak[b]
45	8	4	—	12	13	—	4	6	—	5	—	—	133
46	14	7	—	1	5	—	3	5	—	3	—	5	147
47	12	8	—	1	5	—	2	3	—	3	—	5	147
48	—	—	—	1	15	—	5	4	—	2	—	1	135
49	—	—	9	1	—	13	2	2	9	—	2	9	121
50	4	2	5	2	8	1	—	1	6	1	4	9	229
51	4	2	—	2	7	1	—	1	5	1	5	9	229
52	1	—	—	1	2	—	—	—	2	—	1	—	229
53	2	—	—	—	2	1	—	—	3	—	2	2	257

[a] Me = methyl, Et = ethyl, Pr = *n*-propyl, Pe = *n*-pentyl, C_6H_4 = 1,4-phenyl, C_6H_{10} = 1,4-cyclohexyl.
[b] *m/z* of base peak.
[c] A = 14 (CH_2, compounds **45–47**, **50–53**) or 17 (OH, **48** and **49**).
[d] See *m/z* (76 + R^1).
[e] X = Pr-C_6H_{10}, Y = Pe-C_6H_{10}, Z = C_6H_4CN.

$[H_2C{=}CHC_6H_4CO]^+$ and $[H_3C_3C_6H_4]^+$. The nature of the remaining ions listed is evident.

New mass spectra of various (bi)phenyl esters of (cyclohexyl)benzoic acid derivatives **45–53** (class V) are given in Table 7. Molecular ions are not present, or have abundances <1% (**48**, **52** and **53**). In agreement with the literature cited above,[2,5] the carbonyl ions $[R^1C_6H_4CO]^+$ give the base peaks at *m/z* (104 + R^1), except in the spectrum of **49**, which shows the base peak at *m/z* 121, corresponding to the ion $[HOC_6H_4CO]^+$. The occurrence of abundant *p*-hydroxyphenylcarbonyl ion peaks in the spectra of a few alkoxybenzoates has been reported.[3,5] In the spectra of the alkyl(cyclohexyl)benzoates **45–47** and **50–53**, $[H_2CC_6H_4CO]^{+\cdot}$ ions at *m/z* 118 are found with low abundances. The ester group appears as $[HOC_6H_3R^3R^2]^{+\cdot}$ at *m/z* (92 + R^3 + R^2) in most of the spectra. Ions $[R^1C_6H_4]^+$ at *m/z* (76 + R^1) appear only in the spectra of the alkylbenzoates **45–48**, while peaks at *m/z* 131 are only found for alkylcyclohexylbenzoates.

REFERENCES

1. P. A. Leclercq and H. M. van den Bogaert, *Org. Mass Spectrom.* **25**, 550 (1990).
2. J. Čermák, I. Kolb and I. Nádherná, *Chem. Prum.* **38**, 407 (1988).
3. T. I. Martin and W. E. Haas, *Anal. Chem.* **53**, 593A (1981).
4. H. J. Deutscher, M. Schierhorn, G. Kraus and H. Remane, *Fresenius' Z. Anal. Chem.* **314**, 476 (1983).
5. R. L. Hubbard, in *Proceedings of the Symposium on the Physics and Chemistry of Liquid Crystal Devices*, ed. by G. J. Sprokel, p. 331. Plenum, New York (1979).
6. P. A. Leclercq and H. M. van den Bogaert, *Org. Mass Spectrom.* **26**, 135 (1991).